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EVALUATION OF MEASUREMENT UNCERTAINTY IN ANALYTICAL INORGANIC ASSAYS: A STUDY OF CASE

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Abstract: The uncertainty estimation procedures recommended in ISO-GUM are largely used by several laboratories and institutes. This work compares the ISO-GUM approach and the Monte Carlo simulation method for the Cd concentration uncertainty (U) determination, using the A-5 example showed at EURACHEM Guide. The Monte Carlo simulation showed very similar results in comparison to the ISO-GUM approach. It can be concluded that both methods are applicable for the expanded uncertainty determination and provide reliable results.

Keywords: Monte Carlo simulation, ISO-GUM, uncertainty estimation

1. INTRODUCTION

Science and modern industry demand reliable measurements, which can be achieved by measurement traceability and uncertainty estimation. The estimation of the measurement uncertainty reflects the lack of knowledge of the measurand true value. Measurement uncertainty provides a confidence interval within which the true value lies; it is an estimation of how much the conventional true value is close to the true value [1].

It is convenient to adopt a standard procedure to estimate the measurement uncertainty. The "Guide to Expression of Uncertainty in Measurement (GUM)" published by ISO [2], is recommended by the International Bureau of Weights and Measures (BIPM)[3] and is followed by NIST Guidelines [4] and the rules of the Laboratory of the Government Chemist [5]. EURACHEM/CITAC has also produced a guide that applies the GUM principles to analytical measurements [6].

To establish the uncertainty budget, it is necessary to identify the variables that contribute to uncertainty and their sizes. For chemists, some sources of uncertainty are the measurement of volume, purity of reagents, weighing and reaction temperature. The sources of uncertainty [2] are classified in two different ways called type A evaluation and type B evaluation. The type A evaluation is a method of evaluation of uncertainty by statistical analysis of series of observations [2]. All type A uncertainties must be included in a transparent uncertainty budget. After identifying all the uncertainty components an experienced scientist may disregard minor components if there contribution on the overall uncertainty is very small compared to the main sources of uncertainties. Type B evaluation is a method of evaluation of uncertainty by means other than statistical analysis of series of observations [2], like uncertainties taken from certificates of reagents or glassware.

In order to establish an international consensus for the estimation of measurement uncertainties, the International Organization for Standardization (ISO) has developed and published the Guide to the Expression of Uncertainty in Measurement (ISO-GUM) [2].

Since then, ISO-GUM suggestions have become the most used and accepted method for measurement uncertainty estimation. However, when the modeling equation used for the mensurand determination presents a strong non-linear nature, the overall uncertainty may be underestimated due to limitations of the ISO-GUM suggested method, such as the linear approximation, assumption of normality of the parameter being studied and analytical evaluation of the effective degrees of freedom [7].

In order to overcome these drawbacks, Monte Carlo simulation can be applied to estimate measurement uncertainties by using the concept of propagation of distributions. This concept constitutes a generalization of the law of propagation of uncertainties given by the ISO-GUM, providing a practical solution for complicated models and working with richer information. Therefore, Monte Carlo simulation is attracting interest as a more reliable tool for evaluation of measurement uncertainties as it uses random number generation to simulate values of the involved variables rather than performing analytical calculations. Recently, ISO has published a draft supplement for ISO-GUM that is being developed to provide guidelines for the use of numerical methods for the propagation of distributions, including Monte Carlo simulations [7].

1.1 The Monte-Carlo simulation approach for evaluating measurement uncertainty

According to Herrador et al. [8], the evaluation of the measurement uncertainty by Monte-Carlo simulation can be itemized in the following steps:

(1) Establishment of the model equation for the measurement process between the analytical result Z, and the parameters or individual factors x_i (equivalent to the specification step of GUM approach) as indicated in Eq. (1).

(2) Selection of the significant sources of uncertainty (analogous to the identification step of GUM approach).

(3) Identification of the probability density functions $p(xi)$ corresponding to the uncertainty sources selected.

(4) Selection of the number M of Monte-Carlo trials.

(5) Extraction (simulation) of M samples $\{xi1, xi2, . . . , xiM\}$ of each xi significant uncertainty source, considered as a random variable with a probability density function $p(xi)$.

(6) Computation of the M results $\{Z1, Z2, . . . , ZM\}$ by applying Eq. (1) to the M samples $\{xi1, xi2, . . . , xiM\}$ for each variable xi. From the estimated set of results $\{Z1, Z2, . . . , ZM\}$, the 'combined uncertainty' $u(Z)$ can be calculated now easily as the standard deviation:

$$u(Z) = \sqrt{\frac{\sum_{i=1}^{Z} Z_i^2 - \frac{\left(\sum_{i=1}^{Z} Z_i\right)^2}{M}}{M-1}} \qquad (1)$$

With the advent of the high-speed modern computers, a large number of trials can be processed without time limitations. In case of correlated random variables, e.g. xi and xj, their values are suitably simulated from the joint probability density function p (xi,xj). Once the coverage probability, p, is selected, the confidence interval for the result is evaluated as $\left\lfloor Z_{(1+p)M/2} - Z_{(1-p)M/2} \right\rfloor$ whose extremes correspond to the 2.5 and 97.5% percentiles of the sorted Z values. When the skewness value of the Z forecast discrete distribution is near zero, the confidence interval becomes symmetric and the expanded uncertainty $U(Z)$ can be approximated to

$$U(Z) = \frac{\left\lfloor Z_{(1+p)M/2} - Z_{(1-p)M/2} \right\rfloor}{2} \qquad (2)$$

and the corresponding coverage factor can be back-evaluated as $k = U(Z)/u(Z)$.

2. METHODOLOGY

2.1. Evaluation of Cd Concentration uncertainty using ISO-GUM suggestions

The main uncertainty sources described in Appendix 5 of EURACHEM for cadmium determination by AAS and the approach adopted are detailed below.

The combined uncertainty of the volume flask was calculated through the square root of the squares of 4 components of uncertainty, i. e., the filling (u_{fill}), temperature (u_{temp}), reading (u_{read}) and calibration (u_{cal}).

In the filling component, the measurement uncertainty of 0.5% was assumed and there was not information about the confidence level, so, a triangular distribution was assumed. In the temperature factor, the measurement uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. This coefficient for water is 2.1 x 10^{-4} mL. $^{o}C^{-1}$ which gives a volume variation for a 0.25 L volumetric flask as calculated below:

$u_{temp} = V . T . c$

where V is the volume, T is the temperature and c is the coefficient of expansion of water. There is also a precision of 1% that comes from manufacturer specification.

The calibration component was based in the manufacturer specification and in a triangular distribution.

The rectangular distribution is assumed when the data limits were supplied without a confident level and there are reasons to expect extreme values, however, if there are no reasons to expect extreme values, in general, the triangular distribution is assumed [6].

The calibration standards were measured and the line equation $A_j = C_i .B_1 + B_o$ represent the analytical curve, where A_j j^{th} is the measurement of the degree of absorption from the j^{th} calibration standard, C_i is the concentration of i^{th} calibration standard and B_1 is the angular coefficient and B_0 is the intersection point with Y axis.

The standard uncertainty in relation to the concentration and the residual standard deviation (s) were calculated by the expressions below:

$$u_{C_0} = \frac{s}{B_1} \times \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(C_0 - C)^2}{s_{xx}}} \qquad (3)$$

$$s = \sqrt{\frac{\sum_{j=1}^{n} \left[A_j - (B_0 + B_1 \times C_j\right]^2}{n-2}} \qquad (4)$$

$$s_{xx} = \sum_{j=1}^{n} (C_0 - C)^2 \quad (5)$$

where *p* is the number of the measurements to determine, C_0 n is the number of measurements for the calibration, *C* is the average value of the different calibration standards, *i* is the index for the number of calibration standards and *j* is the index for the number of measurements to obtain the analytical curve [6].

The standard uncertainty in relation to the mass was calculated considering the analytical balance measurement uncertainty used in weighing the sample. ($u_{95} = 2{,}5.10^{-04}$ g).

The combined standard uncertainty was done based on the errors propagation law, by 'root sum squares' of the individual uncertainties [6].

2.2. Evaluation of Cd Concentration uncertainty using Monte Carlo simulation

The first step was to select probability density functions (normal, uniform, triangular, etc) for each quantity used to calculate trace element (Cd) concentration, as well as a dispersion value (standard deviation or interval) for each of them.

Monte Carlo simulation was done by programming Microsoft Excel® to generate pseudo-random probabilities for the distributions of the involved quantities. In this way, possible random values are generated for each quantity, according to their distribution functions. Uniform pseudo-random numbers were generated using the Hill-Wichmann algorithm [9]. In the case of normal distributions, an algorithm for the polar form of the Box-Muller transformation was used [10]. These algorithms were implemented in Excel® by adding new macros. Both are recommended by the ISO-GUM supplement on numerical simulations as suitable for metrology calculations [7]. Values of Cd concentration are then calculated for each iteration according to Eq. 6 and are evaluated statistically in the end of the simulation. A total of 50,000 values of Cd concentration were calculated.

3. RESULTS AND DISCUSSION

In order to estimate the measurement uncertainty based on EURACHEM/CITAC Guide – Quantifying Uncertainty in Analytical Measurement [6], the most relevant sources of measurement uncertainty were identified which contributed in the cadmium concentration in ceramic ware and they are presented in the cause-effect diagram, Figure 1.

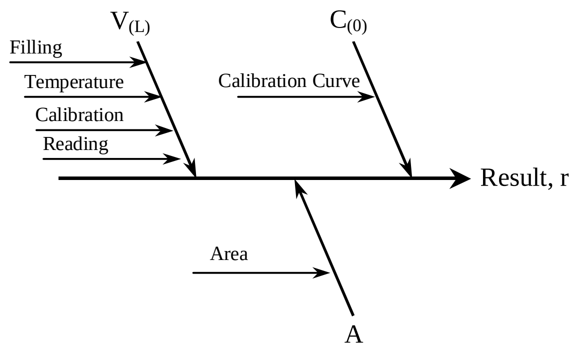

Figure 1. Cause-effect diagram

The measurand r was calculated through the expression

$$r = \frac{C_0 \times V_{(L)}}{A} \times d \times f_{acid} \times f_{temp} \times f_{time} \quad (6)$$

where C_0 is the cadmium concentration (mg. L^{-1}); $V_{(L)}$ is the volume of sample solution (L); A is the area of ceramic (dm^2), d is the dilution factor. To accommodate the additional influence quantities the equation is expanded by the respective correction factors where f_{acid} is the Acid concentration, f_{temp} is the Temperature effect and f_{time} is the Time effect.

Evaluation of Cd concentration uncertainty using Monte Carlo simulation was carried out using a package of Microsoft® Excel for Monte Carlo calculations. The number of trials (*M* = 50,000) was chosen and the simulation was started.

The obtained expanded uncertainty for Cd concentration measurement using the ISO-GUM approach was 0.0068, while the conventional true value obtained analytically was 0.0364. On the other hand, statistics obtained for the frequency distribution histogram for estimated values of Cd by Monte Carlo simulation are presented in Table 1. Considering that the value obtained for distribution skewness is sufficiently near zero to assume a symmetrical distribution, the expanded uncertainty for Cd concentration can be calculated as U = 0.0074.

Table 1. Statistics obtained by Monte Carlo simulation.

Parameter	Value
Mean	0.0364932
Median	0.0364016
Standard deviation	0.0037989
Skewness	0.1798419

Table 2 shows a comparison between results from both methods of uncertainty estimation. As can be seen, comparing combined uncertainties calculated by the classical method and Monte Carlo simulation, the values show that, in this case, there was no significant difference, indicating that the methods can be used.

Table 2. Comparison between ISO-GUM and Monte Carlo simulation uncertainty estimation methods.

	GUM	Monte Carlo
Estimate (Conc.); mg.dm^{-2}	0.0364	0.0365
Expanded uncertainty (U)	0.0068	0.0074

When using Monte Carlo simulation, it is very important to correctly identify the main uncertainty contributions and their respective distributions. On the contrary, incorrect measurement uncertainty estimates could be obtained.

4. CONCLUSION

Credibility of analytical data has never caught the public's eye more than today. The key principle for quality and reliability of results is comparability between laboratories and on a wider, international basis. In order to be comparable, analytical results must be reported with a statement of measurement uncertainty and they must be traceable to common primary references. In this paper, the authors have demonstrated that the results obtained by both uncertainty estimation methods were statistically homogeneous.

ISO-GUM and Monte Carlo uncertainty estimation methods showed very similar results when used for Cd estimation by atomic absorption spectrometric measurements. Monte Carlo simulation may be used to estimate expanded uncertainty of the whole process, since the main uncertainty contributions and their respective distributions are properly identified.

There seems to be a future inclination in the use of Monte Carlo simulation on uncertainty estimations [11]. An ISO-GUM supplementary guide on the use of numerical simulations for the propagation of distributions is being prepared by a working group of the Joint Committee for Guides in Metrology and recognizes that Monte Carlo simulations should be used instead of the typical uncertainty propagation when evaluating measurement uncertainties.

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